Proceedings of the 4th International Conference on Civil Engineering for Sustainable Development (ICCESD 2018), 9~11 February 2018, KUET, Khulna, Bangladesh (ISBN-978-984-34-3502-6)

CHEMICAL FERTILIZERS EFFECT ON ARSENIC LEACHING FROM THE CONTAMINATED SEDIMENT UNDER AEROBIC CONDITIONS

[1]Md. Abul Hashem, [2]Md. Aminur Rahman, [1]Mehedi Hasan, [1]Md. Abdul Momen and [1]Quazi Farjana Lamia

[1] Department of leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh
[2] Department of Public Health Engineering (DPHE), Zonal Laboratory, Khulna-9100, Bangladesh
e-mail:mahashem96@yahoo.com

ABSTRACT

In this work, batch-wise leaching behavior of arsenic from the contaminated sediment by the effect chemical fertilizers especially triple super phosphate (TSP) and diammonium phosphate (DAP) is stated. The split barrel sampler equipment was used to collect sediments from three depth relatively undisturbed sediments. Arsenic content in the designated sediments was 3.63 mg/kg, 8.96 mg/kg, 0.71 mg/kg, respectively. In batch leaching experiment, 2 g sediment sample was added into a reactor containing 25 mL distilled water with different doses of chemical fertilizers: 0.0 (without fertilizers), 0.2, 0.4, 0.6, 0.8 and 1.0 g. Leachates were analyzed by the atomic absorption spectroscopy. Results indicate that arsenic concentration in the leachates was gradually increased with increasing the TSP and DAP doses in the suspension. TSP was extracted more arsenic than DAP from the sediment adsorption sites. It could be said that phosphate fertilizers enhance leach arsenic from the contaminated sediments.

Keywords: *Arsenic, Contamination, Leaching, Sediment, Fertilizers*

1. INTRODUCTION

Arsenic is distributed throughout the rocks, soil, and natural water. Elevated levels of arsenic occur in the environment from the various manmade activities and natural geochemical processes (Kinniburgh & Kosmus 2002; Roussel, Neel, & Bril, 2000). Arsenic occurrence, toxicity, and mobility in groundwater have gained significantly increasing attention (Anawar, Akai, Komaki, Terao, Yoshioka, Ishizuka, Safiullah, & Kato, 2003). Industrialization increases the disposing of mine tailings and metallurgical slags (Jacob & Otte, 2004; Stoltz & Greger, 2006; Ettler, Komarkova, Jehlicka, Coufal, Hradil, Machovic, & Delorme, 2004). Hereafter, the soil is contaminated with toxic heavy metals from where possible mobilization/leaching of metals into groundwater or enter the human food chain. Arsenic is one of the major environmental concerns and excessive exposure to arsenic causes carcinogenic effects in mankind (Baig, Sheng, Hu, Xu, & Xu, 2015).

The toxicity of arsenic is well known (Choong, Chuah, Robiah, Koay, & Azni, 2007). Due to its toxicity, the World Health Organization has categorized arsenic as group 1 carcinogenic element (NRC, 1999). Of course, the toxicity of arsenic depends on its oxidation state, arsenite is more toxic than arsenate (Fazal, Kawachi, & Ichion, 2001). Long-term exposure to arsenic causes arsenicosis, keratosis and cancers of the skin, kidney, and lungs (Tabelin, Igarashi, & Takahashi, 2012). Worldwide in 20 countries groundwater is contaminated with arsenic; the most severely affected countries are Bangladesh, West Bengal (India), Taiwan, Vietnam, Cambodia, Argentina (Naidu, Smith, Owens, Bhattacharya, & Nadebaum, 2006).

The mobility of arsenic from the sediment or soil into groundwater is a great concern. Over-exploitation of groundwater for irrigation, atmospheric oxygen enters into the aquifer where it reacts with the arsenopyrite (Eq. 1), which influences the release of arsenic into the groundwater (Neil, Yang, & Jun, 2012). Application of phosphate fertilizer causes to mobilize arsenic due to anion exchange onto the reactive mineral surfaces (Acharyya, Lahiri, Raymahashay, & Bhowmik, 2000). Phosphate having the smaller in size, higher charge density, therefore, increasing phosphate concentration in the suspension the leached amount of arsenic also increased (Zhang & Magdi, 2008).

$$4FeAsS + 6H_2O + 11O_2 \leftrightarrow 4Fe^{2+} + 4H_3AsO_3 + 4SO_4{}^{2-} \ldots\ldots\ldots\ldots\ldots\ldots(i)$$

Many types of research have investigated the mechanism of geochemical occurrence of arsenic into groundwater but still, the mechanism of arsenic leaching is not clear (Anawar, Akai, Komaki, Terao, Yoshioka, Ishizuka, Safiullah, & Kato, 2003). In the last decades, many researchers have investigated the potential leaching of arsenic from the contaminated sediment/solid with various leaching agents e.g., bicarbonate ion (Anawar, Akai, & Sakugawa, 2004), phosphate ion (Hashem, Toda, & Ohira, 2015), citric solution (Ettler, Komarkova, Jehlicka, Coufal, Hradil, Machovic, & Delorme, 2004), chelating agent (Garrabrants & Kosson, 2000), etc. Miro, Hansen, Chomchoei, & Frenzel (2005) have proposed the protocol of leaching traces metals from the environmental samples. Of course, their attempts were good but unfortunately, most of them used the chemical for leaching tests as analytical grade reagents. It is necessary to examine how arsenic is behaved by the effect of chemical fertilizers. Because it is claimed that application of triple super phosphate (TSP) accelerates to leach arsenic from the sediment/soil to the groundwater.

Here an investigation was done the leaching behavior of arsenic from the contaminated sediment at different depth by the effect of chemical fertilizers especially triple super phosphate (TSP) and diammonium phosphate (DAP) under aerobic conditions. The leachates were analyzed for arsenic by the atomic absorption spectroscopy (AAS).

2. METHODOLOGY

2.1 Sampling

The sediments were collected from the arsenic contaminated area in Kustia district, Bangladesh. Sediments were collected from the different depth from the surface of 165-170 ft., 175-180 ft., and 210-215 ft. The split barrel sampler equipment was used for drilling to collect relatively undisturbed sediments. The sediment was collected into polyethylene and brought back to the laboratory. The granulometric composition of sediment was medium in coarse size and color was yellowish brown. The granulometric content includes gravel and sand.

2.2 Leaching Chemicals and Reagents

Chemical fertilizers: triple super phosphate (Bengal Corporation Ltd., Bangladesh) and diammonium phosphate (Bengal Corporation Ltd., Bangladesh) were collected from the local fertilizer dealer shop, Khulna, Bangladesh. All stock solutions were prepared from the analytical reagents (AR). Freshly prepared double deionized distilled water was used in all experiments. Arsenic (As) standard solutions were procured from Fluka-Analytical, Switzerland. Arsenic trihydride (AsH_3) generation was performed with 5M HCl (Sigma-Aldrich, USA) and 0.6% sodium borohydride solution (Sigma-Aldrich, USA).

2.3 Acid digestion

Total arsenic content in the sediment was determined by the acid digestion followed the standard method (Kagaku 1997). About two (2) gram sediment was digested with 15 mL of nitric acid and 15 mL of doubly diluted sulphuric acid. A 10 mL of nitric acid was added occasionally, and finally, 5 mL of nitric acid and 3 mL of perchloric acid were added and heated until the liquid volume became 5 mL. After cooling at room temperature, 50 mL deionized water (DIW) was added and again heated for 60 min. The resulting suspensions were filtered through the filter paper (Whatman 1) and made up to 100 mL with deionized water.

2.4 Batch leaching test

The collected sediments were air dried at room temperature and finally at 105°C in an oven for 3 h to remove the adsorbed water. Every 2 g sediment sample was added to reactor each containing 25 mL distilled water with six different amounts of fertilizers 0 (no fertilizer), 0.2, 0.4, 0.6, 0.8 and 1.0 g. Air was purged at the flow rate of 20 mL/min since 1 h before the addition of sediment through the solution to make it aerobic and after sediment addition air purging was continued for 1 h. Then, the suspension was filtered through filter paper and leachates were analyzed by AAS. The pH of the solutions was monitored with the pH meter (UPH-314, UNILAB, USA). The schematic diagram of leaching reactor is depicted in Fig. 1.

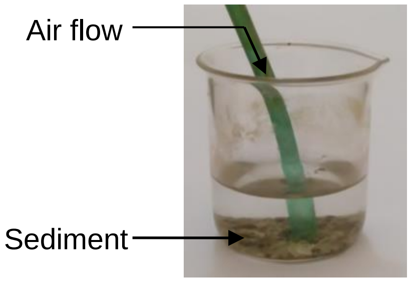

Figure 1: Schematic diagram of reactor for batch leaching test

2.5 Long time leaching test

To investigate the leaching behavior of arsenic from the sediment S2, S3 for a long time by the effect of DAP and TSP; each 4 g sediment was put into the reactor containing 100 mL distilled water. Air was purged at the flow rate of 20 mL/min since 1 h before addition of sediment through the distilled water to make it aerobic and continued until to complete the experiment. Every 6, 12, 24, 36, 48, 72, 96, 120, 144, and 168 h; 3 mL leachates were taken by filtering through the 0.45 µm filter paper. The leachates were measured for arsenic quantification by the AAS.

2.6 Determination of arsenic by AAS

Arsenic quantification of the acid digested aliquots and leachates were determined by the atomic absorption spectroscopy (SpectrAA-220, VARIAN, Australia). The arsenic measurement was performed by the hydride vapor generation (HVG) method. Arsenic trihydride (AsH_3) generation was achieved with 5M HCl (Sigma-Aldrich, USA) and 0.6% sodium borohydride solution (Sigma-Aldrich, USA). Argon was used as carrier gas (0.1 L/min) and measurement was performed at the wavelength of 193.7 nm. The limit of detection was obtained from the three times of the standard deviation of blank responses and the limits of quantification were obtained from the ten times the standard deviation of the blank responses. The detection limit was 0.5 µg/L.

3. RESULTS AND DISCUSSION

3.1. Physical properties and arsenic content in sediments

The granulometric composition of sediment is shown in Fig. 1. The color of the sediment was yellowish brown to gray. The granulometric content contains gravel and sand. Table 1 shows the arsenic content in sediments. Arsenic content in the sediment S1, S2, and S3 were 3.63 mg/kg, 8.96 mg/kg, and 0.71 mg/kg, respectively.

Figure 2: Physical appearance of sediment samples from different depth

It seems from the Table 1 that sediments are highly contaminated with arsenic. The arsenic could leach from the contaminated sediment into groundwater that could be a risk for human health. Remediation of the sediment or soil is one of the possible ways of stopping arsenic leaching.

Table 1: Arsenic content in the sediments

No.	Sample	Depth (feet)	Arsenic (mg/kg)
01	S1	165-170	3.63
03	S2	175-180	8.96
06	S3	210-215	0.71

3.2 Batch leaching test with TSP and DAP

Leaching of arsenic from the sediments by the effect of TSP and DAP under aerobic conditions is shown in Fig. 2. It is clear that the amount of leached arsenic from the sediment was gradually increased with increasing the number of chemical fertilizers of TSP and DAP in the suspensions. The leached amount of arsenic from the sediment was significantly related to the chemical fertilizers of TSP and DAP.

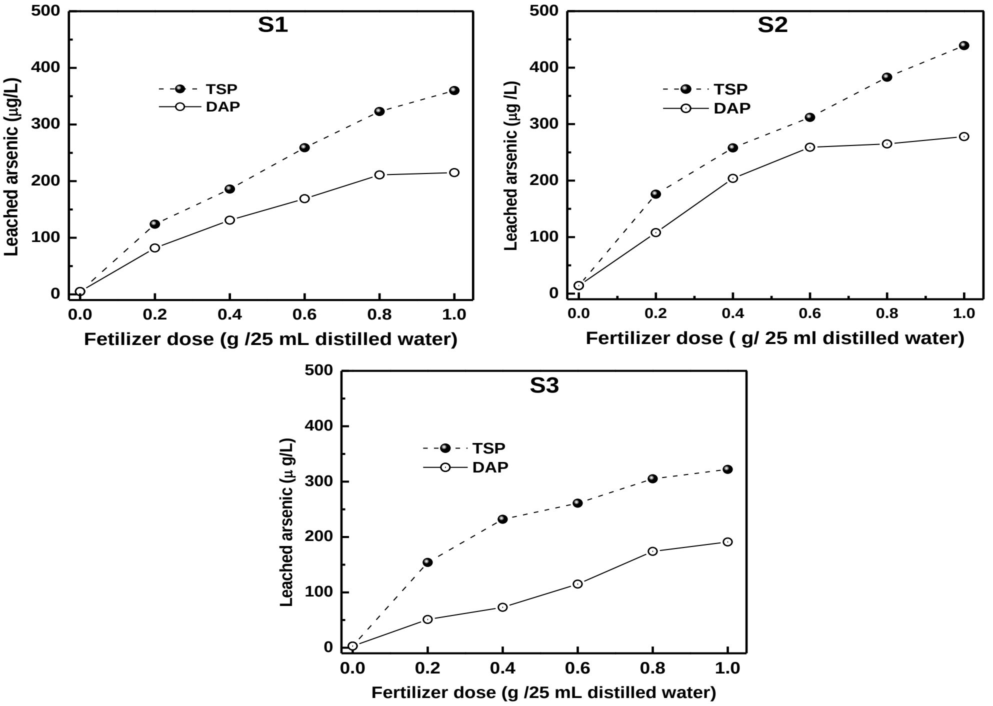

Figure 3: Batch leaching test with TSP and DAP under aerobic conditions. Every 2 g sediment samples each containing 25 mL distilled water in different fertilizers doses 0 (no fertilizer), 0.2, 0.4, 0.6, 0.8 and 1.0 g.

The leached amount of arsenic from the sediments was obviously related to the chemical fertilizers of TSP and DAP. Leaching amount of arsenic was gradually increased for each sediment samples S1, S2, and S3 with increasing the TSP in the suspension. It is also noticeable that the higher arsenic content in sediments; the higher amount of arsenic was leached from the sediments in the aqueous phases. For example, arsenic was contained in S1 and S2 sediment 3.63 mg/kg and 8.96 mg/kg, respectively. By the effect of TSP at 1.0 g/25 mL distilled water under aerobic condition, leached arsenic was 360 µg/L and 439 µg/L, respectively. In case of S3, arsenic contains in sediment was 0.71 mg/kg but the leached amount of arsenic was 322 µg/L, which was comparatively higher than the leached amount of arsenic from the sediment samples S1 and S2. It may be the reason, S3 was contained more leachable arsenic than S1 and S2.

Arsenic leaching from the sediment samples S1, S2, and S3 with increasing the DAP in the aqueous phase. It is clear from the Fig. 2 that leaching amount of arsenic was increased with increasing DAP concentration in the aqueous phase. Like TSP effect on arsenic leaching, arsenic as leached from the S1, S2 and S3 by the effect of DAP at 1.0 g/25 mL distilled water under aerobic condition 215 µg/L, 278 µg/L and 191 µg/L, respectively. It is also noticeable that although arsenic content in S1 and S2 was 5.1 and 12.6 times higher than in S3 leached amount of arsenic was comparatively more from the S3 by the effect of DAP under aerobic condition. It may be the reason that S3 had more leachable arsenic.

3.3 Long time leaching with TSP and DAP

Long-term leaching of arsenic from the sediment S2 and S3 by the effect of DAP and TSP under aerobic conditions is depicted in Fig. 3. It seems that up to 72 h, leached amount of arsenic in the aqueous phase was almost same by the effect of DAP and TSP. Afterwards, the leached amount of arsenic was varied from each other of sediment S2 and S3. At 96 h and 120 h, leached arsenic was 686 µg/L and 926 µg/L for S2 and 563 µg/L and 649 µg/L for S3 by the effect of DAP and TSP.

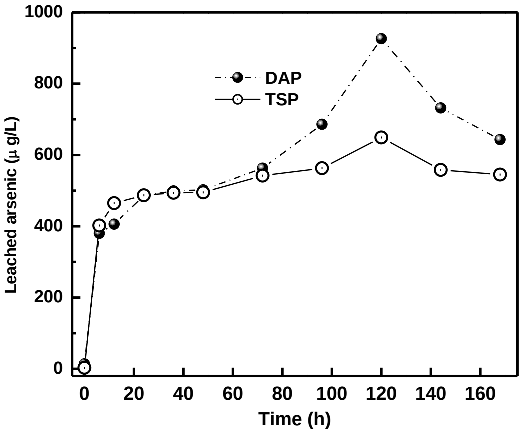

Figure 4: Long-term leaching of arsenic for sediment S1 and S2 by the effect of TSP and DAP under aerobic conditions.

After 120 h, leached amount of arsenic was gradually decreased. It may the reason that arsenic was readsorbed on the sediment surface. In sediment S2, arsenic was contained 12.6 times higher than S3 but the leached amount of arsenic in aqueous was relatively high. Possibilities are **i**) S3 was contained more leachable arsenic and **ii**) TSP was extracted more arsenic from the adsorption sites of sediment S3.

Both the TSP and DAP produce phosphate ion in the suspension therefore with increasing the TSP and DAP more arsenic was desorbed from the adsorption site from sediment. As phosphate (PO_4^{3-}) has higher charge density than arsenate (AsO_4^{3-}) consequently leached amount of arsenic was increased with increasing the TSP and DAP in the suspension (Violante & Pigna, 2002).

4. CONCLUSIONS

These study results reveal that chemical fertilizers can effectively leach arsenic from the selected sediment under aerobic condition. With increasing the chemical fertilizers doses in the suspension leached amount of arsenic was also increased. Triple super phosphate was effective extract arsenic from sediment adsorption sites than diammonium phosphate. It could be said that chemical fertilizers leach arsenic from the contaminated sediments or soil

REFERENCES

Anawar, H. M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S., & Kato, K. (2003). Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *Journal of Geochemical Exploration*, 77,109–131.

Anawar, H. M., Akai, J., & Sakugawa, H. (2004). Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere*, 54(6), 753–762.

Acharyya, S.K., Lahiri, S., Raymahashay, B.C., & Bhowmik, A. (2000). Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environmental Geology*, 39 (10), 1127-1137.

Baig, S. A., Sheng, T., Hu, Y., Xu, J., & Xu, X. (2015). Arsenic Removal from Natural Water Using Low Cost Granulated Adsorbents: A Review. *Clean–Soil, Air, Water*, 43 (1), 13–26.

Choong, T. S. Y., Chuah, T. G., Robiah, Y., Koay, F. L.G., & Azni., I. (2007). Arsenic tox-icity, health hazards and removal techniques from water: an overview. *Desalination*, 217, 139–166.

Ettler, V., Komarkova, M., Jehlicka, J., Coufal, P., Hradil, D., Machovic, V., & Delorme, F. (2004). Leaching of lead metallurgical slag in citric solutions-implications for disposal and weathering in soil environments. *Chemosphere*, 57, 567–577.

Fazal, M. A., Kawachi, T., & Ichion, E. (2001). Extend and severity of groundwater arsenic contamination in Bangladesh. *Water International*, 26(3), 370–379.

Garrabrants, A. C., & Kosson. D. S. (2000). Use of a chelating agent to determine the metal availability for leaching from soils and wastes. *Waste Management*, 20,155–165.

Hashem, M. A., Toda, K., & Ohira, S. I. (2015). Leaching behavior of arsenite and arsenate from the contaminated sediment by the effect of phosphate ion under anaerobic conditions. *Environ Earth Sciences*, 74, 737–743.

Jacob, D. L., & Otte, M. L. (2004). Influence of Typha latifolia and fertilization on metal mobility in two different Pb–Zn mine tailings types. *The Science of the Total Environment,* 333, 9–24.

Kagaku Jikken Tekisuto Kenkyukai (Ed.), HeavyMetals in Sediments (Pretreatments) (in Japanese), KankyoKagaku, Sangyo Tosho Co., Tokyo, 1997, pp. 66–73.

Kinniburgh, D. G., & Kosmus, W. (2002). Arsenic contamination in groundwater: some analytical considerations. *Talanta*, 58,165–180.

Miro, M., Hansen, E. H., Chomchoei, R., & Frenzel, W. (2005). Dynamic flow-through approaches for metal fractionation in environmentally relevant solid samples. *TrAC Trend in Analytical Chemistry*, 24(8), 759–771.

Naidu, R., Smith, E., Owens, G., Bhattacharya, P., & Nadebaum, P. (2006) Managing Arsenic in the Environment from Soil to Human Health. CSIRO Publishing. p. 3.

Neil, C. W., Yang, Y. J., & Jun, Y-S. (2012). Arsenic mobilization and attenuation by mineral-water interactions: implications of for managed aquifer recharge. *Journal of Environmental Monitoring,* 14, 1772–1778.

NRC (1999). National Research Council Report: Arsenic in Drinking Water, National Academy of Sciences, Washington, DC.

Roussel, C., Neel, C., & Bril, H. (2000). Minerals controlling arsenic and lead solubility in an abandoned gold mine tailings. *The Science of the Total Environment*, 263, 209–219.

Stoltz, E., & Greger, M. (2006). Release of metals and arsenic from various mine tailings by *Eriophorum angustifolium*. *Plant Soil*, 289, 199–210.

Tabelin, C. B., Igarashi, T., & Takahashi, R. (2012). Mobilization and speciation of arsenic from hydrothermally altered rock in laboratory column experiments under ambient conditions. *Applied Geochemistry*, 27, 326–342.

Violante, A., Pigna, M. (2002). Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil Science Society of America Journal, 66, 1788–1796

Zhang, H., & Selim, M. (2008). Competitive sorption-desorption kinetics of arsenate and phosphate in soils. *Soil Science*. 173(1), 3–12.